CLAIMS

What is claimed is:

1. A method of preparing a polymeric brush substrate for use in solid-phase synthesis of macromolecules, the method comprising:

(a) providing a substrate to which one or more free radical initiators are covalently attached, wherein each free radical initiator has a radical generation site distal to the substrate; and

(b) contacting the covalently attached substrate with monomers under conditions that promote free radical polymerization from the radical generation sites of the initiators to form a polymeric brush.

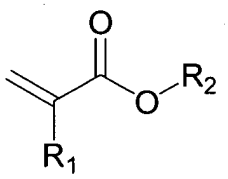
2. The method of claim 1, wherein step (b) comprises living free radical polymerization.

3. The method of claim 1, wherein the substrate comprises glass or silica.

4. The method of claim 1, wherein the monomers comprise a vinyl group.

5. The method of claim 4, wherein the monomers include at least two different monomers.

6. The method of claim 1, wherein the monomers independently have the structure:



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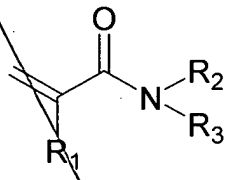


wherein R_1 is hydrogen or lower alkyl; and

R_2 and R_3 are independently hydrogen, alkyl, alkoxy, hydroxyalkyl, polyalkylene oxide, or —Y—Z, wherein Y is linear or branched lower alkyl, aryl, alkylaryl, or polyalkylene oxide, and Z is hydrogen, hydroxyl, alkoxy, carboxy, amino, hydrazino, sulfydryl, or C(O)—R, where R is hydrogen, hydroxy, lower alkoxy or aryloxy.

7. The method of claim 1, wherein the polymer brush formed on the support comprises hydroxyl, amino, carboxyl, or sulfydryl groups or a combination thereof.

8. The method of claim 1, wherein the monomers comprise vinyl acetate.

9. A method for affixing functional sites to a surface of a solid substrate, the method comprising:

(a) providing a substrate to which one or more free radical initiators are covalently attached, wherein each free radical initiator has a radical generation site distal to the substrate; and

(b) contacting the substrate with a mixture of linking monomers and diluent monomers under conditions that promote free radical polymerization from the radical generation sites of the initiators to produce a brush polymer comprising functional sites, wherein the density of the functional sites is determined by the ratio of functional monomers to diluent monomers.

10. The method of claim 9, wherein the linking monomers comprise a vinyl group.

11. The method of claim 9, wherein the linking monomers comprise at least two different linking monomers.

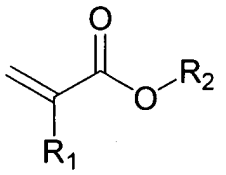
12. The method of claim 9, wherein the initiator is an azo type initiator.

13. The method of claim 9, wherein the functional sites are selected from the group consisting of amino, hydroxyl, carboxyl or sulfydryl.

14. The method of claim 9, wherein the ratio of linking monomers to diluent monomers is from about 1:2 to about 1:200.

15. The method of claim 9, wherein the ratio of linking monomers to diluent monomers is from about 1:2 to about 1:2000.

16. The method of claim 9, wherein the monomers independently have the structure:



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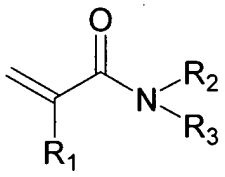

wherein R_1 is hydrogen or lower alkyl; and

R_2 and R_3 are independently hydrogen, alkyl, alkoxy, hydroxyalkyl, polyalkylene oxide, or —Y—Z, wherein Y is linear or branched lower alkyl, aryl, alkylaryl, or polyalkylene oxide, and Z is hydrogen, hydroxyl, alkoxy, carboxy, amino, hydrazino, sulfydryl, or C(O)—R, where R is hydrogen, hydroxy, lower alkoxy or aryloxy.

17. The method of claim 9, wherein the substrate comprises glass or silica.

18. A substrate capable of supporting macromolecular array synthesis, the substrate comprising polymer brushes formed by free radical polymerization, wherein said polymer brushes comprise hydroxyl, amino, or carboxyl, groups or a combination thereof.

19. The substrate of claim 18, wherein the density of the polymer brushes is 0.1 to 1000 pmoles of individual polymer chains per cm^2 of substrate surface area.

20. The substrate of claim 18, further comprising an array of macromolecules attached to polymeric brushes on the substrate.

21. The substrate of claim 20, wherein the macromolecules comprise polynucleotides.